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NEW MONO- AND BI-DESMOSIDIC TRITERPENOIDS ISOLATED FROM *COMBRETUM PADOIDES* LEAVES

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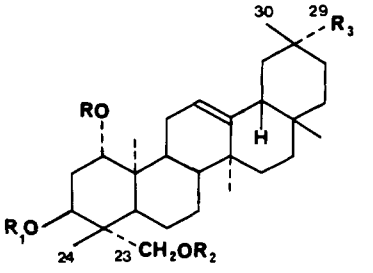
ABSTRACT.—The extracts of the leaves of *Combretum padoides* were examined. The isolation of five new triterpenoid desmosides and 25(27)-dehydroporiferasterol from the leaves of *C. padoides* is reported.

In a previous paper (1), the structures of 23-hydroxyimberbic acid 23-*O*-α-L-rhamnoside [**1**] and its 1-acetate, two new triterpenoid rhamnosides, were described from the leaves of *Combretum imberbe*. Earlier studies of *Combretum* species have yielded mollic acid glucoside, an anti-inflammatory and antifungal agent from *Combretum molle* (2), and imberbic acid from *C. imberbe* (3). Both compounds have been identified as potent molluscicides.[1] More recently a tlc survey of the *Combretum* genus (4) has revealed the presence of saponins in the leaves of *Combretum padoides* Eng. & Diebs (Combretaceae). This paper describes the isolation and structural elucidation of five new triterpenoid desmosides from this species.

Air-dried leaves from an inland and a coastal specimen of *C. padoides* were extracted separately as described in a previous paper (3), and the fractions from the petroleum ether and Et_2O extracts were subjected to exhaustive chromatography. Although the chemical profiles of the extracts from the coastal and inland trees were essentially the same, the compounds in the polar fractions of the Et_2O extract differed, and consequently each extract was examined separately. Three new compounds, **2**, **3**, and **4**, were iso-



	R	R_1	R_2	R_3
1	H	H	Rh	CO_2H
7	Ac	Ac	$RhAc_3$	CO_2H
2	H	H	4-AcRh	CO_2H
8	Ac	Ac	$RhAc_3$	CO_2H
3	H	Rh	4-AcRh	CO_2H
9	Ac	$RhAc_3$	$RhAc_3$	CO_2H
4	H	Rh	Rh	CO_2H
5	H	Rh	4-AcRh	CH_2OH
10	Ac	$RhAc_3$	$RhAc_3$	CH_2OAc
6	H	Rh	Rh	CH_2OH

Rh = α-L-rhamnopyranosyl

[1]Prof. K. Hostettmann, University of Lausanne, Switzerland, 1987, personal communication.

lated from leaves of the inland specimen and another two, **5** and **6**, from leaves collected from the coastal specimen.

From spectroscopic data it was clear that compound **1** and compound **2** (molecular formula $C_{38}H_{60}O_{10}$ consistent with ms spectral data) were closely related, differing only in the ^{13}C-nmr resonances of the sugar carbons and by the presence of an acetyl group in **2** (ir bands at 1734 cm^{-1}, ^{1}H-nmr signal at δ 1.95, and ^{13}C-nmr signals at δ 20.8 and 170.4). Since both compounds have identical aglycones (see ^{13}C-nmr data in Table 1) and both have rhamnose as their sugar moiety (acid hydrolysis and co-chromatography), the acetyl group in **2** must be located on the rhamnose moiety and consequently this compound must be the monoacetate of **1**. Peracetylation of **2** gave the pentaacetate **8** which was identical with the pentaacetate **7** given by **1** (Table 1), thus confirming this relationship.

The location of the acetyl group on **2** was fixed at C-4′ by ^{13}C nmr. A comparison of the sugar resonances in the spectra of **1** and **2** showed that C-1′ and C-2′ were unchanged, whereas C-3′ and C-5′ have both shifted upfield by 2.6 and 3.7 ppm, respectively (typical β-acetylation shifts), C-4′ has shifted downfield by 1.8 ppm (a typical α-acetylation shift), and C-6′, the methyl carbon, has shifted upfield by 0.6 ppm. These values are a perfect fit for an acetate at C-4′, and **2** must be 23-hydroxyimberbic acid 23-*O*-α-L-4-acetylrhamnopyranoside.

The remaining four compounds were more polar (tlc) than **2**, and it was obvious from the various spectra that they contained more than one sugar moiety. Of the two further compounds **3** and **4** from the inland specimen, **3** was the less polar and the more abundant. It formed the heptaacetate **9** under mildly forcing conditions, and on the basis of ms spectral evidence it had a molecular composition of $C_{44}H_{70}O_{14}$. A comparison of the ^{13}C-nmr data for **2** and **3** (Table 1) revealed that these compounds differed only in the C-2, C-3, and C-23 resonances and in the number of sugar carbon signals present. Two anomeric carbon signals at δ 100.8 and 103.8 in the spectrum of **3** confirmed the presence of two sugar units both of which were shown to be rhamnose by acid hydrolysis and co-chromatography (tlc). This evidence suggested two possibilities: either the sugar units were attached to ring A as a disaccharide unit, or **3** was a bidesmoside with the two rhamnose units attached at C-3 and C-23. The following showed the latter to be true.

A comparison of the C-2, C-3, and C-23 resonances in the ^{13}C-nmr spectra of **2** and **3** (Table 1) showed that these carbons in the spectrum of **3** have experienced shifts of −2.1 ppm, +10.1 ppm, and −1.0 ppm, respectively, typical of glycosylation shifts at C-3 (3). The small upfield shift experienced by C-23 can be attributed to γ-gauche shielding due to a sugar at C-3; therefore, C-23 must still be linked to a sugar moiety. In addition, the chemical shifts for the 23-methylene protons in the AB system have changed from δ 2.87 and 3.51 in the ^{1}H nmr spectrum of **8** to δ 3.11 and 3.66 in the spectrum of **9**. This change in environment around C-23 and resultant deshielding are to be expected if glycosylation has occurred at C-3. Finally, it is possible to assign all the sugar carbon signals to a structure comprising a rhamnose moiety at C-3 and a 4-*O*-acetyl rhamnose moiety at C-23 (Table 1). Compound **3** is therefore 23-hydroxyimberbic acid 3β-*O*-α-L-rhamnopyranosyl-23-*O*-α-L-4-acetylrhamnopyranoside. Compound **4**, which had the molecular composition $C_{42}H_{68}O_{13}$ (from ms spectral data), was the minor and most polar constituent of the extract. Except for the sugar region and the absence of resonances for an acetate function, the ^{13}C-nmr spectrum of **4** (Table 1) was identical with that of **3**, i.e., they had the same aglycone. Both sugars in **4** were found to be rhamnose (acid hydrolysis and co-chromatography), which explained the sugar resonances in the ^{13}C-nmr spectrum. Apart from the two anomeric carbon signals at δ 101.3 and 103.8, the sugar carbon signals from each rhamnose moiety were

TABLE 1. ^{13}C-nmr Spectra of Compounds **1–6** and Peracetates **7–10**.

Carbon	Compound									
	1[a]	**2**[a]	**3**[a]	**4**[a]	**5**[a]	**6**[a]	**7**[b]	**8**[b]	**9**[b]	**10**[b]
C-1	71.4	71.3	71.1	71.2	71.0	71.2	73.5	73.5	74.1	74.1
C-2	35.1	35.0	32.9	32.9	33.0	33.0	27.2	27.2	28.8	28.7
C-3	66.5	66.7	76.8	76.9	76.8	77.1	69.5	69.6	77.4	77.4
C-4	42.4	42.5	42.4	42.4	42.4	42.5	41.0	41.0	42.1	42.1
C-5	40.9	40.6	40.5	40.6	40.5	40.8	41.2	41.2	41.5	41.4
C-6	18.2	18.3	18.1	18.1	18.1	18.1	17.8	17.8	17.7	17.7
C-7	32.0	32.0	32.0	32.0	31.9	31.9	31.3	31.4	31.4	31.4
C-8	39.7	39.7	39.6	39.6	39.6	39.6	39.5	39.6	39.6	39.5
C-9	38.1	38.1	38.1	38.0	38.1	38.1	38.0	38.0	38.2	38.2
C-10	42.6	42.6	42.5	42.5	42.4	42.4	39.7	39.7	39.7	39.6
C-11	23.4	23.4	23.5	23.5	23.3	23.4	22.9	23.0	23.0	22.9
C-12	122.7	123.1	123.3	123.4	122.5	122.5	122.4	122.4	122.5	121.9
C-13	144.4	144.1	144.2	144.3	144.9	145.1	143.7	143.4	143.7	144.3
C-14	41.1	41.0	40.8	40.7	40.7	40.8	41.7	41.8	41.8	41.8
C-15	25.9	26.4	26.4	26.1	26.4	26.3	26.0	26.1	26.1	26.1
C-16	27.1	27.0	27.0	27.0	27.0	27.1	26.7	26.7	26.7	26.6
C-17	32.6	32.6	32.6	32.5	33.0	33.0	32.2	32.2	32.2	32.6
C-18	46.5	46.4	46.4	46.4	46.8	46.8	45.6	45.6	45.6	45.8
C-19	41.2	41.3	41.3	41.3	41.7	41.6	40.1	39.9	40.0	41.0
C-20	42.6	42.4	42.4	42.3	36.5	36.6	42.4	42.4	42.4	34.6
C-21	29.6	29.5	29.6	29.3	29.5	29.3	28.7	28.8	28.8	29.1
C-22	36.3	36.2	36.2	36.2	36.5	36.6	35.7	35.7	35.7	35.7
C-23	71.4	70.5	69.5	69.6	69.6	69.6	69.8	69.8	70.2	70.2
C-24	12.8	12.7	12.9	12.9	12.8	13.0	12.8	12.9	12.4	12.3
C-25	16.9	16.8	16.8	16.8	16.8	16.9	15.9	15.9	16.0	16.8
C-26	17.2	17.2	17.2	17.1	17.1	17.2	16.7	16.8	16.8	16.8
C-27	26.2	25.9	25.9	25.9	25.9	26.8	25.5	25.6	25.6	25.5
C-28	28.2	28.2	28.3	28.2	28.4	28.5	27.9	28.0	28.0	28.0
C-29	181.1	180.8	181.0	181.1	69.7	69.9	184.3	184.7	184.6	68.7
C-30	19.7	19.7	19.7	19.6	19.4	19.4	19.0	19.0	19.0	19.0
C-1′	101.6	101.1	100.8	101.3	100.8	101.3	97.5	97.6	97.0	96.9
C-2′	72.1	71.9	72.0	72.1	71.9	72.2	69.6	69.5	69.5	69.5
C-3′	72.8	70.2	70.1	72.6	70.1	72.5	68.9	68.9	68.9	68.8
C-4′	73.4	75.3	75.3	73.3	75.2	73.9	71.0	71.0	71.0	71.1
C-5′	69.6	65.9	66.8	69.6	66.8	69.6	66.4	66.5	66.4	66.3
C-6′	18.4	17.6	17.6	18.1	17.5	18.1	17.2	17.2	17.1	17.0
C-1″			103.8	103.8	103.8	103.6			99.6	99.5
C-2″			72.2	72.1	72.2	71.9			69.0	68.9
C-3″			72.6	72.6	72.6	72.5			69.0	68.9
C-4″			73.9	73.8	73.8	73.9			71.2	71.1
C-5″			69.5	69.5	69.5	69.6			66.4	66.3
C-6″			18.1	18.1	18.1	18.1			17.1	17.0

[a]Measured in pyridine-d_5 relative to TMS.
[b]Measured in $CDCl_3$ relative to TMS.

superimposed on one another to give five two-carbon signals which matched α-rhamnose signals in known compounds (5). Consequently, **4** is 23-hydroxyimberbic acid 3β-*O*-α-L-rhamnopyranosyl-23-*O*-α-L-rhamnopyranoside and **3** is its 4-*O*-monoacetate. This relationship was confirmed by the conversion of **3** into **4** by base hydrolysis. Hydrolysis also caused the ^{13}C-nmr signal of the anomeric carbon attached to C-23 to shift by 0.5 ppm, whereas the anomeric carbon attached to C-3 is unchanged. This is additional evidence that the monoacetylated rhamnose moiety is situated at C-23 rather than at C-3.

The oxidation state of the C-29 carbon was shown to be the principal difference between the previous compounds and the two compounds, **5** and **6**, isolated from the coastal *C. padoides*. In particular, ^{13}C-nmr analysis showed that in both **5** and **6** the C-29 carboxy carbon signal at δ 181.0 had been replaced by a hydroxymethylene carbon signal at δ 69.6, and the carbons in ring D, and in particular C-20 (−5.9 ppm), had experienced shifts consistent with this change. In addition, the ^{1}H-nmr spectrum of the octaacetate **10** formed on peracetylation of **5** exhibited a two-proton doublet at δ 3.71, typical of an equatorially oriented CH_2OAc group (6), and in the ir spectrum the shoulder at 2650 cm^{-1} due to the CO_2H dimer was absent. A closer inspection of the ^{13}C-nmr spectra (Table 1) showed that the difference at C-29 was the only one between compounds **5** (molecular composition $C_{44}H_{72}O_{13}$ from ms spectral data) and **3**, and consequently **5** must be 1α,3β,23,29-tetrahydroxy-olean-12-ene 3-*O*-α-L-rhamnopyranosyl-23-*O*-α-L-4-acetylrhamnopyranoside. A similar comparison showed that compound **6**, the minor, more polar compound, differed from **5** by an acetate group and was the reduced equivalent of **4**; therefore its structure must be 1α,3β,23,29-tetrahydroxy-olean-12-ene 3-*O*-α-L-rhamnopyranosyl-23-*O*-α-L-rhamnopyranoside.

From the unusually bright blue colors it formed with tlc spray reagents, it was obvious that the phytosterol fraction in the petroleum ether extract did not consist of the usual mixture (sitosterol, campesterol, and/or stigmasterol) found in *Combretum* extracts. Cc on Si gel and recrystallization yielded crystals of 25(27)-dehydroporiferasterol [stigmasta-5,22(*E*),25(27)-trien-3β-ol], identified by spectroscopy and not previously isolated from *Combretum* species. The distinctive blue color developed with *p*-anisaldehyde/concentrated H_2SO_4 spray reagent suggested that this compound could prove a useful chemotaxonomic marker for *C. padoides* species.

Also of chemotaxonomic significance is the difference between the oxidation states at C-29 in the compounds isolated from coastal and inland trees. These differences could be due to geographic or genetic factors and need to be investigated further. Also of interest is the pairing of the compounds **3** and **4** and compounds **5** and **6**; tlc showed that **2** was also paired with trace quantities of a more polar compound that could not be isolated but that co-chromatographed with and therefore could be **1**, i.e., the deacetylated equivalent of **2**. In each pair the monoacetylated compound was the more abundant with the deacetylated compound occuring in trace amounts.

EXPERIMENTAL

INSTRUMENTATION.—Melting points are uncorrected. Ir spectra were recorded from KBr discs on a Shimadzu IR-460; ^{1}H and ^{13}C nmr were recorded on a Varian FT-80. Ms spectra were obtained on a Finnigan MAT 90 mass spectrometer and optical rotations measured with a Perkin-Elmer 221 spectrophotometer. Tlc analysis was carried out on aluminum-backed Merck Si gel GF_{254} plates.

PLANT MATERIAL.—*Inland.*—Leaves were collected in January 1987 from trees growing in the National Botanic Gardens, Pretoria, South Africa.

Coastal.—Leaves were collected in February 1988 from a tree in Durban, Natal, South Africa grown from a seed collected in 1977 from a *C. padoides* tree growing in the National Botanic Gardens, Harare, Zimbabwe.

Inland and coastal voucher specimens have been deposited in the Roddy Ward Herbarium, University of Durban-Westville.

EXTRACTION AND PURIFICATION.—Dried, milled leaf material (350 g inland trees, 250 g coastal trees) was extracted as previously described (3). The petroleum ether extract (5 g) was separated by Si gel cc using petroleum ether-EtOAc (8:3) as eluent. Fractions containing the phytosterol were combined and recrystallized from EtOH to give 25(27)-dehydroporiferasterol (80 mg), identified from mp, ms, ^{1}H-nmr (7), and ^{13}C-nmr (8) data.

The polar fractions of the petroleum ether extracts were purified by cc as described previously (1) to yield compounds **2–6**.

23-HYDROXYIMBERBIC ACID 23-*O*-α-L-4-ACETYLRHAMNOPYRANOSIDE [**2**].—Compound **2** (350 mg): mp 240–244° (dec); $[\alpha]^{25}D$ +8.9 (1.33, pyridine); ir ν max cm^{-1} 3420, 3245, 2965, 2650 (CO_2H dimer), 1737 (acetate), 1703–1685 (carboxy CO), 1459, 1384, 1254, 1229 (acetate), 1126, 1106, 1054–1036, 962; ^1H nmr (pyridine-d_5) δ 1.95 (3H, s, OAc); ^{13}C nmr see Table 1; eims *m/z* (rel. int.) 658 $[M-H_2O]^+$ (8), [M − rhamnose acetate]$^+$ 469 (5), [RDA fragment] 248 (100), [RDA fragment] 203 (25), [rhamnose acetate fragment] 188 (95); fabms $[M+Na]^+$ 699.

ACETYLATION OF **2**.—Compound **2** (150 mg) was dissolved in 5 ml Ac_2O and 1 ml pyridine and heated (100°) for 2 h. The reaction mixture was allowed to stand for 12 h at 24°. The usual workup produced needles of an acetate **8** crystallized from EtOH (158 mg): mp 189–192°; $[\alpha]^{25}D$ +22.6° (1.22, $CHCl_3$); ir ν max cm^{-1} 2962, 2650 (CO_2H dimer), 1742–1730 (acetate, carboxy CO), 1372, 1250–1224 (acetate), 1133, 1082, 1041, 976; ^1H nmr ($CDCl_3$) δ 0.78–1.22 (7 × Me), 1.92, 1.96, 2.01, 2.13 (5 × OAc), 2.87 (1H, d, J = 9.8 Hz, H-23a), 3.51 (1H, d, J = 9.9 Hz, H-23b), 3.80 (m, H-5′), 4.61 (1H, br s, H-1′), 4.72 (1H, dd, $J_1 = J_2 = 3$ Hz, H-1β), 5.02–5.37 (m, 4H-2′, 3′, 4′, 12); ^{13}C nmr see Table 1; eims *m/z* (rel. int.) $[M]^+$ 844 (17), $[M-HOAc]^+$ 784 (66), $[M-HOAc-CO_2H]^+$ 739 (45), $[M-2\times HOAc]^+$ 724 (33), $[M-2\times HOAc-CO_2H]^+$ 679 (25), 540 (30), 451 (35), [rhamnose] 273 (100), [RDA fragment] 248 (35), [RDA fragment] 203 (43).

23-HYDROXYIMBERBIC ACID 3-*O*-α-L-RHAMNOPYRANOSYL-23-*O*-α-L-4-ACETYLRHAMNOPYRANOSIDE [**3**].—Crystals from EtOH/EtOAc (220 mg): mp 250–255.9° (dec); $[\alpha]^{25}D$ −15.7° (c = 1.34, pyridine); ir ν max cm^{-1} 3435, 2930, 2650 (CO_2H dimer), 1735 (acetate), 1705, 1458, 1381, 1255, 1227 (acetate), 1127, 1075–1039, 976; ^1H nmr (pyridine-d_5) δ 1.96 (3H, s, OAc); ^{13}C nmr see Table 1; fabms $[M+H]^+$ 823, $C_{44}H_{70}O_{14}$ requires $[M]^+$ 822.

ACETYLATION OF **3**.—Compound **3** (85 mg) was dissolved in 3 ml Ac_2O and 1 ml pyridine, heated (100°) for 2 h, and left to stand overnight. Workup in the usual way afforded the heptaacetate **9** as crystals from EtOH (80 mg); mp 233–238°; $[\alpha]^{25}D$ +5.2° (c = 1.22, $CHCl_3$); ir ν max cm^{-1} 2930, 2650 (CO_2H dimer), 1743–1720, (acetate, carboxy CO), 1371, 1243–1222 (acetate), 1132, 1082, 1046, 976; ^1H nmr ($CDCl_3$) δ 0.78–1.24 (8 × Me), 1.94, 1.98, 2.02 (6H, s), 2.08, 2.12 (6H, s) (7 × OAc), 3.11 (1H, d, J = 9.8 Hz, H-23a), 3.62 (1H, d, J = 9.8 Hz, H-23b), 3.8 (2H, m, H-5′, H-5″), 4.60–4.80 (3H, m, H-1′, H-1″, H-1), 5.00–5.37 (7H, m, H-2′, 2″, 3′, 3″, 4′, 4″, H-12); ^{13}C nmr see Table 1; eims *m/z* (rel. int.) $[M]^+$ 1074 (11), 892 (21), 725 (24), 705 (12), 550 (26), 522 (26), [rhamnose] 273 (100), 213 (100); $C_{56}H_{82}O_{20}$ requires $[M]^+$ 1074.

BASE HYDROLYSIS OF **3**.—Compound **3** (60 mg) was refluxed in 10 ml 10% methanolic KOH until tlc showed complete conversion of **3** had taken place. The reaction solution was diluted with H_2O and acidified, and the precipitate was collected and recrystallized from EtOAc/EtOH to give crystals (35 mg) shown by mp, ir and ^{13}C nmr to be identical with compound **5**.

23-HYDROXYIMBERBIC ACID 3-*O*-α-L-RHAMNOPYRANOSYL-23-*O*-α-L-RHAMNOSIDE [**4**].—Crystals from EtOAc (25 mg); mp 272–274° (dec); ir ν max cm^{-1} 3440, 2925, 2645 (CO_2H dimer), 1696 (carboxy CO), 1447, 1382, 1206, 1121, 1099–1045, 977; ^{13}C nmr see Table 1; fabms $[M+Na]^+$ 803, $[M-18-146]^+$ 616; $C_{42}H_{68}O_{13}$ requires $[M]^+$ 780.

1α,3β,23,29-TETRAHYDROXYOLEAN-12-ENE 3-*O*-α-L-RHAMNOPYRANOSYL-23-*O*-α-L-4-ACETYLRHAMNOPYRANOSIDE [**5**].—Compound **5** (65 mg): mp 256–261°; $[\alpha]^{25}D$ +17.9° (c = 1.0, MeOH); ir ν max cm^{-1} 3425, 2920, 1724 (acetate), 1448, 1381, 1250, 1139, 1075–1043, 976; ^1H nmr (pyridine-d_5) δ 2.00 (3H, s, OAc); ^{13}C nmr see Table 1; fabms $[M+Na]^+$ 831; $C_{44}H_{72}O_{13}$ requires $[M]^+$ 808.

ACETYLATION OF **5**.—Compound **5** (40 mg) was acetylated in the usual way and the octaacetate **10** crystallized from EtOH (33 mg): mp 220–222°; $[\alpha]^{25}D$ +10.9° (c = 1.0, $CHCl_3$); ir ν max cm^{-1} 2920, 1741 (acetate CO), 1445, 1363, 1248–1216 (acetate), 1126, 1077, 1041, 974; ^1H nmr ($CDCl_3$) δ 0.72–1.18 (8 × Me), 1.88, 1.92, 1.96 (6H, s), 1.98, 2.01, 2.06 (6H, s), 3.10 (1H, d, J = 9.8 Hz, H-23a), 3.62 (partially obscured 1H, d, H-23b), 3.71 (2H, d, J = 2.3 Hz, 2 × H-29), 3.80 (2H, m, H-5′,5″), 4.72–4.81 (3H, m, H-1β, H-1′,1″), 5.00–5.35 (7H, m, H-12, H-2′, 2″, 3′, 3″, 4′, 4″); ^{13}C nmr see Table 1.

1α,3β,23,29-TETRAHYDROXYOLEAN-12-ENE 3-*O*-α-L-RHAMNOPYRANOSYL-23-*O*-α-L-RHAMNOPYRANOSIDE [**6**].—Colorless glass from EtOAc/MeOH (29 mg): $[\alpha]^{25}D$ +14.0° (c = 1.0, MeOH); ir ν max cm^{-1} 3425, 2920, 1447, 1381, 1205, 1080–1042, 976; ^{13}C nmr see Table 1.

ACID HYDROLYSIS: GENERAL METHOD.—Each compound (10 mg) was refluxed with 5 M HCl in MeOH (5 ml) until tlc showed the hydrolysis was complete. Workup and identification of the sugar were carried out as previously described (1).

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